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This final report summarizes the findings of an extensive study in injection molding of engineering plastics. Two engineering plastic resins, i.e. unmodified grades of a poly(ether imide) and a poly (2,6-dimethyl-1,4-phenylene ether) were thoroughly characterized. The characterization included rheological, thermal and P-V-T behavior. The data were employed to predict various microstructural distributions including density, residual stress and birefringence distributions in compression and injection molded specimens of these two engineering plastics. The detailed microstructural distributions were also studied experimentally upon processing the two engineering plastics, employing instrumented machines and industrial practices. The experimental findings were elucidated under the light of the numerical simulation results. Overall, this study should furnish a first order understanding of the microstructure development in articles injection molded from amorphous engineering plastic resins.			
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INJECTION MOLDING OF ENGINEERING PLASTICS

FINAL REPORT

Dilhan M. Kalyon
Professor

March 1, 1991

U. S. Army Research Office
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Stevens Institute of Technology
Castle Point, Hoboken, N.J. 07030



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I. Foreword:

This final report summarizes the findings of a research project in the area of injection molding of engineering plastics. The U.S. Army Research Office grant consisted solely of a fellowship to one Ph.D. student including his stipend and tuition. We were able to leverage this source of funding with an additional unrestricted grant from GE Corporation. We are grateful to the U. S. Army Research Office for making this study possible.

The findings of this project are very well documented in terms of published articles. Six papers appeared in the literature and two additional manuscripts are still pending. Furthermore, other integral aspects of this research not funded by ARO also appeared in a number of publications. Thus, this report will be limited only to our major findings and the ramifications of these findings. The details of the work can be found in the papers, reprints of which were sent to ARO Library. Further information can be obtained by contacting me directly:

Professor Dilhan M. Kalyon
Chemistry and Chemical Engineering
Stevens Institute of Technology
Castle Point, Hoboken, NJ 07030
Tel: (201) 420-5725
Fax: (201) 420-5601

II. Statement of the Problem Studied:

The injection molding of engineering plastics which can be used in various DoD applications currently suffers from the lack of predictability of the properties of the molded articles. The relevant ultimate properties including mechanical and optical properties are functions of the microstructure developed during the molding cycle, which in turn is related to the thermo-mechanical history experienced by the resin on one hand and the properties of the resin, on the other hand. However, for these materials to be considered truly "engineering" their properties need to be known apriori.

Our study was an integrated study, in which state-of-the-art numerical and experimental tools were employed to study every facet of the injection molding of engineering plastics including the microstructure development and the properties of the injection molded articles.

The overall view of the project is shown in Figure 1.

OVERALL VIEW OF INJECTION MOLDING PROJECT

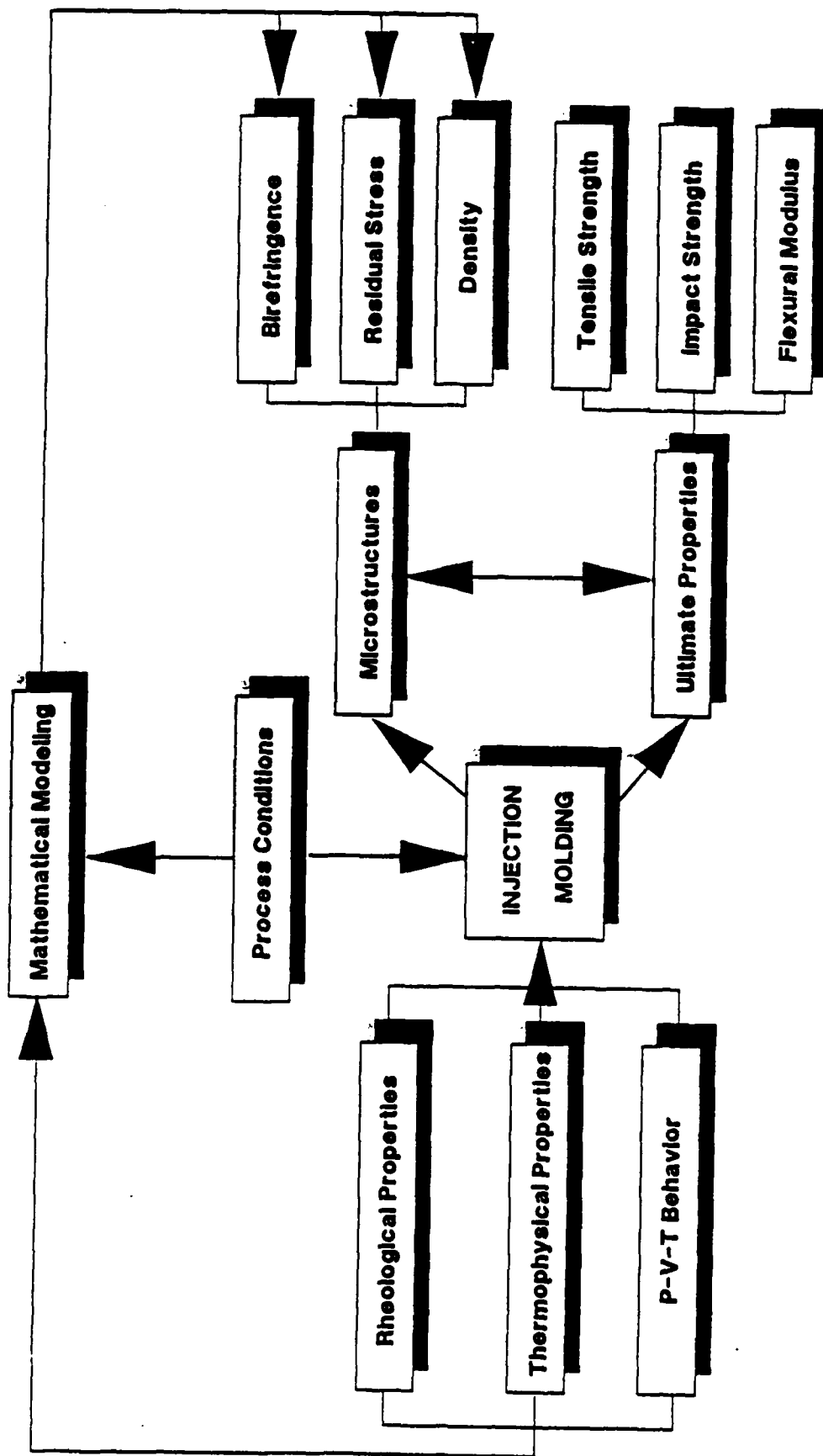


Figure 1.

Scope and Project Objectives:

The present work is the first integrated study which attempts to characterize various material properties, microstructure and ultimate properties in injection moldings of amorphous engineering plastic resins. It aims to develop various first order mathematical models to elucidate the relationship between various material properties, processing conditions and microstructure and ultimate properties of molded articles.

Specific Project Objectives

The specific aims and objectives of this project are summarized in the following.

- (1) To characterize the various shear material functions of two engineering plastic resins including the steady shear viscosity and first normal stress coefficient, storage and loss moduli, growth and relaxation of shear stress and first normal stress coefficient, relaxation moduli upon a step change in shear strain.
- (2) To select a nonlinear viscoelastic constitutive equation which accurately describes the various shear material functions characterized and determine the material parameters of the selected constitutive equation.
- (3) To characterize the thermal properties and P-V-T behavior of the two resins under a wide range of temperatures, to be used in the analysis of cooling process.
- (4) To measure the specific volume as a function of time under isothermal conditions, using dilatometry and determine the thermal expansion coefficient in the glassy state.

- (5) To produce injection molded specimens of the two engineering plastic resins at various molding conditions with acceptable quality. To acquire on-line data on various processing variables such as cavity pressure, melt temperature, nozzle pressure, mold temperature as a function of process time, with the aid of computerized data acquisition system.
- (6) To produce compression molded samples to isolate the effect of thermal history alone on the microstructure development.
- (7) To measure birefringence, residual stress and density distributions of molded specimens in the thickness direction (from skin to core) .
- (8) To characterize the effect of pressure on the density development by developing a technique where the pressure is kept constant during solidification.
- (9) To characterize the effect of cooling rate on the density by cooling specimens under various rates of cooling.
- (10) To develop first order mathematical models to predict various elements of the microstructure including the birefringence, residual stress and density distributions in compression molded and injection molded specimens.
- (11) To compare the predictions with the experimental findings.

This complete knowledge-base for the two resins, established on the basis of these diversified characterization studies encompassing various material properties, microstructure and ultimate properties should be very useful resources for future studies. Together with the developed mathematical model, they should also improve the understanding of processing-structure-property relationship in injection molding of amorphous engineering plastic resins.

III. Summary of the Most Important Results

The present study has integrated extensive experimental data on two engineering thermoplastics with the parallel development of the mathematical models mainly concerning the microstructure development in injection moldings of the two resins. This project was initiated by the interesting observation that the injection moldings of poly(phenylene ether) had an affinity to crack in the absence of external loading but poly(ether imide) did not. To find an answer as to why only injection molded specimens of poly(phenylene ether) crack, extensive experimental data were collected on the behavior of the two engineering plastic resins. The injection moldings of the two resins were also prepared by systematically varying the operating conditions of melt and mold temperatures and injection speed. For poly(phenylene ether), the hopper and the cavity of the injection molding machine were modified to accommodate purging with inert gases to protect the resins from oxidative degradation. In addition, the two engineering plastics were also vacuum-compression molded and subsequently cooled at various cooling rates, in order to facilitate the understanding of the effect of the thermal history alone on the microstructure development. A complete knowledge-base was constructed by integrating the diverse experimental findings on the microstructure development in both injection moldings and compression molded specimens and thus providing insights into the mathematical models. The vast amount of information collected made it possible to draw several conclusions. They are summarized as follows.

(1) A side by side comparison of the two engineering plastic resins were made in various shear material functions. During characterization, poly(phenylene ether) required the use of a nitrogen environment because of its tendency to degrade by a rapid oxidation reaction at elevated temperatures. Furthermore, thermal degradation above 250 °C necessitated that the rheological data could be collected at relatively low temperature range and deformation rates, while these resins are commonly processed at higher temperatures and deformation rates. To gain insight into the processing behavior of the two engineering plastics, the Wagner constitutive equation was employed. The material parameters of relaxation spectra and the damping function of the Wagner model were determined from the dynamic oscillatory shear flow with small amplitude and the step strain experiment under various shear strains, respectively. The Wagner model with the determined material parameters in conjunction with the temperature shift factor allowed the predictions of the

various material functions for typical operating conditions, under which the rheological characterization was unattainable. The two resins exhibited significant differences in their stress relaxation behavior. Poly(ether imide) was found to relax faster than poly(phenylene ether). This significant difference in the stress relaxation was related to the birefringence distributions of the specimens injection molded from these two resins.

(2) Both the birefringence and the residual stress distributions in quenched compression molded specimens indicated that the stresses are compressive and high near the surface and tensile and low in the core. A cross over point from compressive to tensile residual stresses was found at a depth of 16 to 21 percent from the surface. For slow cooling rates, the birefringence distributions were flat with values close to zero, suggesting that the developed residual stresses in the specimens were negligibly small. The residual stress distribution predicted by the thermoelastic theory in conjunction with the experimentally determined heat transfer boundary condition was in good agreement with the experimental data.

(3) The residual stress distributions in the injection molded specimens revealed the presence of compressive stresses at the surface and tensile stresses in the core. The level of residual stresses found in injection molded specimens were significantly lower than those of compression molded quenched samples. The transition from compressive to tensile stresses was found to be at approximately 20 percent from the specimen surface. Under similar mold temperature and injection speed, poly(phenylene ether) exhibited significantly higher compressive stresses at the surface and slightly higher tensile stresses in the core. Increasing injection speed tended to increase both the tensile and compressive residual stress values while maintaining the same compressive/tensile crossover point.

(4) The use of an inert gas during injection molding and the limited changes in the operating conditions had no statistically significant influence on either the birefringence or the ultimate properties. The value of birefringence found in injection moldings of the two resins were close. The higher stress optical coefficient of PEI suggested a higher degree of molecular orientation in PPE at similar values of birefringence. This was also confirmed by the mathematical modeling in

conjunction with realistic material and physical properties. The higher birefringence values near the surface of the specimens were predicted well by the model, while the birefringence in the core could not be predicted. The birefringence values determined in the core was related to the unrelieved thermally induced stresses.

(5) Sharp discontinuities were found in the injection molded specimens of PPE and the location of the discontinuity coincided with the location of cracks, subsequently developed in injection moldings of PPE.

(6) The density distributions in both quenched and injection molded specimens of PPE exhibited greater density values at the surface than at the core. However, poly(ether imide) specimens exhibited minimum density values at the surface with the density values increasing toward the core. The significant differences in the observed density distributions were explained in terms of the competing effect of cooling rate and stress/pressure. The higher value of the pressure induced densification rate of PPE determined from the densification experiment, where the pressure was kept constant during cooling from the rubbery state to the solid state, indicated that the effect of stress or pressure on the density development is more pronounced for PPE.

(7) The mathematical model based on the fictive temperature theory was able to predict the observed density distributions in compression molded and quenched specimens of PEI i.e., lower density at the surface and higher density in the core. The increasing tendency of density with decreasing cooling rate was found from the independent experiments carried out on thin specimens. However, the observed density distributions of PPE could not be explained by the model. This was attributed to the limitations of the model, which did not take into account the effect of the thermally induced stresses.

(8) The observed density distributions in injection moldings of both engineering plastic resins could not be predicted by the existing theory which considered the effect of pressure only on density. A new phenomenological model to predict the density distributions in the injection molded specimens

was proposed integrating both cooling rate and pressure effects. The proposed model was able to predict the observed density distributions reasonably well.

Overall, this study should generate a first order understanding of the microstructure development in the injection molding of amorphous engineering plastics and the role played by the properties of the resin.

Ramifications of the Findings:

- This study suggests that the microstructural distributions in injection molded engineering plastic articles are predictable provided that the right tools are employed.
- The development of premature cracks and their locations could be explained.
- With the developed tools it should be possible to design components with desired profiles in refractive indices etc., opening up very new avenues of commercial applications.

IV. List of All Publications and Technical Reports

- A. H. Wagner and D. M. Kalyon, "Formation of Cracks in Injection Molded Amorphous Engineering Plastics," *Society of Plastics Engineers, ANTEC Technical Papers*, 36 (1990) 1468-1472.
- A. Wagner, J. Yu and D. M. Kalyon, "Injection Molding of Engineering Plastics," *Adv. Polym. Techn.*, 9, 1 (1989) 17-32.
- J. S. Yu, D. M. Kalyon and A. H. Wagner, "Simulation of Microstructure Development in Injection Molding of Amorphous Engineering Plastics," *Society of Plastics Engineers ANTEC Technical Papers*, 35 (1989) 281-285.
- A. H. Wagner, J. S. Yu and D. M. Kalyon, "Orientation and Residual Stress Distributions in Injection Molded Engineering Plastics," *Society of Plastics Engineers ANTEC Technical Papers*, 35 (1989) 303-307.
- A. Wagner, J. Yu and D. M. Kalyon, "Microstructure and Ultimate Properties of Injection Molded Amorphous Engineering Plastics: Poly(ether Imide) and Poly (2,6-Dimethyl-1,4-Phenylene Ether)," *Polymer Engineering and Science*, 29, 18 (1988) 1298-1307.
- D. M. Kalyon, A. Wagner and S. Dey, "Microstructure Development in Injection Molded Engineering Plastics," *Society of Plastics Engineers ANTEC Technical Papers*, 34 (1988) 605-608.
- J. S. Yu, A. H. Wagner and D. M. Kalyon, "Simulation of the Microstructure Development in Injection Molded Amorphous Engineering Plastics," accepted to appear in *Journal of Applied Polymer Science*.
- A. H. Wagner and D. M. Kalyon, "Development of Cracks in Injection Molded Amorphous Engineering Plastics," submitted to *Polym. Eng. Sci.*, January 1990.

Related publications which are not supported by the U.S. Army Research Office:

- J. S. Yu, M. Lim and D. M. Kalyon, "Characterization and Simulation of Density Distributions in Injection Molded Amorphous Engineering Plastics," *Society of Plastics Engineers, ANTEC Technical Papers*, 36 (1990) 313-317.
- D. M. Kalyon, D. Yu and J. Yu, "Melt Rheology of Two Engineering Thermoplastics: Poly(ether Imide) and Poly (2,6-dimethyl-1,4 phenylene Ether)," *Journal of Rheology*, 32, 8 (1988) 789-811.
- J. S. Yu, M. Lim and D. M. Kalyon, "Development of Density Distributions in Injection Molded Amorphous Engineering Plastics: Part I," *Polym. Eng. Sci.*, Mid-February 1991, Vol. 31, No.3.
- J. S. Yu and D. M. Kalyon, "Development of Density Distributions in Injection Molded Amorphous Engineering Plastics: Part II," *Polym. Eng. Sci.*, Mid-February 1991, Vol. 31, No.3.

V. List of Participating Personnel

Dr. D. M. Kalyon, Professor and Principal Investigator

Mr. A. H. Wagner, Ph.D. Student

Due to family reasons, Mr. Wagner had to discontinue his Ph.D. studies and went back to work at American Cyanamid and he is currently studying part-time towards his Ph.D.

Mr. T. Fiske, Ph.D. Student

Mr. Fiske filled Mr. Wagner's position. Since the funding from ARO ran out, he is currently being funded from industrial funds and is studying towards his Ph.D.